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(54) **Method for waterproofing leather**

(57) The present invention provides an aqueous composition for use in waterproofing leather containing an aqueous dispersion of a silicone oil emulsified with a water-insoluble amphiphilic copolymer formed from 50 weight percent to 90 weight percent of at least one ethylenically-unsaturated hydrophobic monomer and from 10 weight percent to 50 weight percent of at least one

copolymerizable water-soluble ethylenically-unsaturated acidic or basic hydrophilic comonomer; where the copolymer has a weight average molecular weight of from 2000 to 100,000; and where the ratio of silicone oil to amphiphilic copolymer by weight is from 1:5 to 8:1. A method for waterproofing leather using the aqueous composition is also provided.

Description

This invention relates to a method for waterproofing leather. This invention also relates to a composition suitable for use in waterproofing leather. More particularly, this invention relates to a method for waterproofing tanned leather by treating the leather with an aqueous dispersion of a silicone oil emulsified with a water-insoluble amphiphilic copolymer.

The present invention is involved with wet end leather processing which takes place after primary tanning, usually "chrome tanning", has been completed. The method of this invention is practiced before, during, or after retanning the leather in order to provide enhanced waterproofing relative to that provided by the same amount of the amphiphilic polymer alone and, especially, enhanced waterproofing with firmness similar to that obtained by treating the leather with the amphiphilic copolymer alone or in conjunction with waterproofing fatliquors.

U.S. Patent No. 4,701,269 discloses a process for waterproofing leather and skins with a silicone oil and a salt of N-(C₉-C₂₀ acyl)amino acid as a non-polymeric emulsifier for the silicone oil, which is carried out in the aqueous phase during or after retanning.

U.S. Patent No. 5,316,860 discloses a method for making leather water-resistant by treating tanned leather with an aqueous dispersion of a water-insoluble dispersed amphiphilic copolymer.

The problem faced by the inventors is the provision of a method for waterproofing leather using an aqueous dispersion of a silicone oil emulsified with a water-insoluble amphiphilic copolymer.

In a first aspect of the present invention there is provided a method for waterproofing tanned leather by treating said leather with a composition comprising from 0.5 to 20 weight percent solids based on the weight of said leather of an aqueous dispersion of a silicone oil emulsified with a water-insoluble amphiphilic copolymer, said copolymer formed from 50 weight percent to 90 weight percent, based on the weight of said copolymer, of at least one ethylenically-unsaturated hydrophobic monomer selected from monomers consisting of hydrophobic alkyl (meth)acrylates; primary alkenes; vinyl esters of alkyl carboxylic acids; vinyl alkyl ethers; dialkyl esters, alkyl ester N-alkylamides, diN-alkylamides, hemi alkylesters, or hemi N-alkylamides of unsaturated dicarboxylic acids; and from 10 weight percent to 50 weight percent, based on the weight of said copolymer, of at least one copolymerizable water-soluble ethylenically-unsaturated acidic or basic hydrophilic comonomer; wherein said copolymer has a weight average molecular weight of from 2000 to 100,000; and wherein the ratio of silicone oil to amphiphilic copolymer by weight is from 1: 5 to 8:1. In a second aspect of the present invention there is provided an aqueous composition for use in waterproofing leather.

This invention relates to the use of an aqueous dispersion of silicone oil dispersed with a selected amphiphilic copolymer as a waterproofing leather treatment. The silicone oil is dispersed in an aqueous medium, an "aqueous medium" defined herein as one containing more than 50% water. The aqueous dispersion of silicone oil of this invention is substantially free from non-polymeric surfactants and contains lower organic solvent concentrations than silicone oil dissolved in a water-miscible solvent as practiced in the industry or than when the amphiphilic solution copolymers dissolved in at least one water-miscible solvent are used alone to achieve the same degree of waterproofing.

"Silicone oils" as used herein refers to polysiloxanes, substituted polysiloxanes, and mixtures thereof. Suitable are polysiloxanes in which the residual valencies of the silicon are satisfied by hydrocarbon radicals such as, for example, methyl, ethyl, propyl, and phenyl or by functionalized hydrocarbon radicals such as, for example, amino, thiol, or carboxy functional radicals. Preferred are silicone oils having a viscosity of from 25-1000 cSt., Preferred are commercial silicone oils identified as dimethylpolysiloxanes and silicone oils ("MQ" resins) formed by combining mono- and tetra- SiO-functional units dissolved in dimethylpolysiloxanes.

The amphiphilic copolymer must contain at least one hydrophobic and at least one hydrophilic group. The copolymer is formed from 10 percent by weight to 50 percent by weight of at least one hydrophilic monomer and from 50 percent by weight to 90 weight percent of at least one hydrophobic comonomer (All weight percents are based on the weight of the amphiphilic copolymer). It is preferred that the copolymer is formed from 15 percent by weight to 45 percent by weight of at least one hydrophilic monomer and 55 percent by weight to 85 weight percent of at least one hydrophobic comonomer, and even more preferred that the copolymer is formed from 20 percent by weight to 40 percent by weight of at least one hydrophilic monomer and 60 percent by weight to 80 weight percent of at least one hydrophobic comonomer.

The hydrophilic monomer used to prepare the amphiphilic copolymer is at least one monomer selected from water soluble ethylenically unsaturated, preferably monoethylenically unsaturated, acidic or basic monomers or mixtures thereof. Examples of suitable hydrophilic monomers include acrylic acid; methacrylic acid; itaconic acid; fumaric acid; maleic acid; and anhydrides of such acids; acid substituted (meth)acrylates, such as for example, phosphoethyl methacrylate and sulfoethyl methacrylate; acid substituted (meth)acrylamides such as, for example, 2-acrylamido-2-methylpropylsulfonic acid; and basic substituted (meth)acrylates and (meth)acrylamides, such as for example, amine substituted methacrylates including dimethylaminoethyl methacrylate, tertiary butyl-aminoethylmethacrylate, and dimethylaminopropyl methacrylamide and the like. The preferred water soluble hydrophilic monomers used to prepare the amphiphilic copolymer are acrylic acid and methacrylic acid.

The selection of the hydrophilic monomer and its level was made to enable the amphiphilic copolymer to function as a dispersant for silicone oil in the continuous phase, such as for example in water, and to enable the aqueous dispersion of silicone oil to be prepared at a high solids content such as, for example, 50% solids at a handleable or shearable viscosity without adversely affecting the ability of the dispersion to penetrate the leather.

The hydrophobic comonomer(s) used to prepare the amphiphilic copolymer includes at least one monomer selected from hydrophobic alkyl (meth)acrylates; primary alkenes; vinyl esters of alkyl carboxylic acids; vinyl alkyl ethers; dialkyl esters, alkyl ester N-alkylamides, diN-alkylamides, hemi alkylesters, or hemi N-alkylamides of unsaturated dicarboxylic acids, and mixtures thereof. Suitable hydrophobic monomers include C₄ to C₂₂ alkyl acrylates; C₄ to C₂₂ alkyl methacrylates; C₄ to C₂₄ 1-alkenes, vinyl esters of C₄ to C₂₂ alkyl carboxylic acids, vinyl C₄ to C₂₂ alkyl ethers, and di C₄ to C₂₂ alkyl esters, C₄ to C₂₂ alkyl ester N-C₄ to C₂₂ alkylamides, diN-C₄ to C₂₂ alkylamides, hemi C₄ to C₂₂ alkylesters, or hemi N-C₄ to C₂₂ alkylamides of unsaturated dicarboxylic acids. The preferred hydrophobic monomers which have been found to provide the amphiphilic copolymer with the best performance characteristics are the C₄ to C₂₂ alkyl (meth) acrylates and mixtures thereof.

The use of the term "(meth)" followed by another term such as acrylate or acrylamide, as used throughout the disclosure, refers to both acrylates or acrylamides and methacrylates and methacrylamides, respectively.

Minor amounts of other ethylenically unsaturated copolymerizable hydrophobic monomers at levels less than 50 weight percent of the total hydrophobic comonomer concentration may be used in combination with a predominant amount (greater than 50 weight percent) of at least one of the above-listed hydrophobic comonomers. These other hydrophobic comonomers have been found to be useful as diluents for the other hydrophobic comonomers without adversely affecting the retan/fatliquor properties obtained upon treatment with the treating composition. Examples of such useful copolymerizable hydrophobic diluent comonomers include styrene, methylstyrenes, vinyl acetate, (meth) acrylonitrile, N-alkyl(meth)acrylamides, and olefins.

The amphiphilic copolymer may be prepared by the polymerization of the hydrophilic and hydrophobic monomers by any conventional polymerization technique such as, for example, solution polymerization, emulsion polymerization and melt bulk polymerization. Polymerization of amphiphilic copolymers using conventional emulsion polymerization is taught in U.S. Patent No. 5,348,807, using a water soluble free radical initiator at a concentration of from 0.1 weight percent to 3 weight percent based on the total monomer weight. The polymerization is preferably conducted at a temperature of from 40 degrees C to 100 degrees C, preferably from 50 to 70 degrees C, using a chain transfer agent, such as for example a mercaptan, to control the molecular weight. Polymerization of amphiphilic copolymers using conventional solution polymerization in a water-miscible solvent is taught in U.S. Patent No. 5,316,860, using a water insoluble free radical initiator such as, for example, peresters and azo compounds at a concentration of from 0.2 weight percent to 5 weight percent on total monomer weight. The polymerization is preferably conducted at a temperature of from 60 degrees C to 150 degrees C, preferably from 85 to 120 degrees C, using a chain transfer agent, such as for example a mercaptan, to control the molecular weight.

The weight average molecular weight of the amphiphilic copolymer useful in the method of the invention can be as low as 2000 to as high as 100,000 weight average molecular weight, preferably less than 50,000. The weight average molecular weight herein is that determined by Gel Permeation chromatography. The polymerization may be conducted by polymerizing all monomers together or by the gradual addition of monomers until polymerization is essentially complete. Residual unreacted monomers can be incorporated into the polymer by the addition of subsequent initiator by techniques well known in the art. The polymerization produces a concentration of amphiphilic polymer solids of 20 % solids to 75 % solids. The amphiphilic copolymers exemplified in the illustrative examples presented hereinafter were made according to the processes described in Example 1 of U.S. Patent No. 5316,860 for solution copolymers or Example 1 of U.S. Patent 5,348,807 for emulsion copolymers, by varying the selection and proportion of monomers and the relative amount of chain transfer agent to obtain different molecular weight polymers.

Emulsifying the silicone oil with the selected amphiphilic copolymer is accomplished by mixing the silicone oil and amphiphilic copolymer under low shear conditions such as by shaking a closed container containing the ingredients by hand. The mixing may be carried out on ingredients which have been heated; typically the ingredients are heated in a hot water bath to a temperature of 60° C. When the amphiphilic copolymers are semi-solid or waxy materials it is preferred to heat the components to insure adequate fluidity for effective dispersion. Optionally, water miscible solvents such as, for example, the butyl ether of ethylene glycol and the butyl ether of propylene glycol may be incorporated to improve fluidity; preferred is the absence of organic solvents due to solvent emission restrictions. Added non-polymeric surfactants are not required to effect the emulsification of the silicone oil. "Emulsification" herein is defined as achieving a uniform appearance which is retained for greater than 30 minutes, i.e., no stratification occurs during that time. Preferred are compositions which retain a uniform appearance, i.e., remain dispersed, for 10 days or more. More preferred are compositions which retain a uniform appearance, i.e., remain dispersed, for 10 days at 60 degrees C., an accelerated test simulating 1-2 year dispersion stability.

The treatment process of the invention involves contacting the leather with the treatment composition containing the aqueous dispersion of silicone oil. The composition used to treat the leather contains from 0.5 to 20 weight percent

solids (silicone oil + amphiphilic copolymer) aqueous dispersion based on weight of leather, preferably in the range of from 1 to 5 weight percent and most preferably in the range of from 1 to 2 weight percent. The ratio of silicone oil to amphiphilic copolymer by weight is from 1: 5 to 8:1. Preferred is a ratio of silicone oil to amphiphilic copolymer by weight is from 1: 3 to 4:1.

5 The treatment composition may contain retanning agents, fatliquors, amphiphilic copolymers and other conventional adjuvants in addition to the aqueous dispersion of silicone oil. In the event that additional amphiphilic copolymer is used, typically for reasons of economics, the total amount of amphiphilic resin is in the range of from 0.5 to 20 weight percent solids based on leather weight, preferably from 2 to 15 weight percent solids based on leather weight.

10 Experimental Methods

Maeser Flex:

One test used for determining the degree of waterproofing of leather was a dynamic saline water resistance test. 15 This test used a Maeser water penetration tester according to ASTM D-2099-70. The number of Maeser flexes needed to cause water to penetrate the leather was recorded. A Maeser flex value of greater than 15,000 is the minimum criterion established by the U.S. military for waterproof boot leather.

% Water uptake:

20 A second test used for determining the degree of waterproofing of leather was a water uptake test. A 5.1 cm by 5.1 cm. (2 inches by 2 inches) leather sample was weighed. It was then placed in a 1 L jar with 10 times its weight of water and tumbled for 30 minutes. The leather was then removed and placed between two rigid plates the same size as the leather each of which has a square of paper blotter disposed between the plate and the leather. A 1 kilogram 25 weight was placed on the top of the assembly for 5 minutes. The weight was removed the assembly was turned over and the weight applied to the top of the inverted assembly for an additional 5 minutes. The leather was then removed from the assembly and reweighed. The weight % water uptake based on the dry weight of the leather on duplicate samples was reported. % Water uptake of 30% or less is acceptable as an industry standard.

30 Softness:

Softness was determined by temper measurements. Readings were made using a BLC ST300 Softness Tester (British Leather Confederation, Northampton, United Kingdom).

35 Preparation of leathers procedure:

The leathers were prepared using the following procedure. Note that some of the steps have treatments that are specific to each Example to follow. Unless otherwise noted, all leathers were prepared using 1.58-1.74 kg./m.² (5.0-5.5 ounce/ft.²) (approximately 2-2.5 mm. thick) chrome tanned cowhides. The procedure is applicable to other types of 40 hides and skins such as mineral (chrome, aluminum, zirconium, titanium, magnesium) tanned animal substrates such as pigskin, sheepskin, and the like. All weights are based on the weight of the bluestock (100% means a weight equal to the weight of the stock in the drum).

- 1). The bluestock was given a water wash with the drum door open for 15 minutes at 40° C.
- 45 2). The drum was then drained.
- 3). The bluestock in 200% float was neutralized with 2% sodium acetate and a certain amount of sodium bicarbonate specific to each Example. See each Example for the specific amount of sodium bicarbonate that was used. This neutralization step was done at 40° C for 2.5 hours.
- 4). The drum was then drained and its temperature increased to 50° C.
- 50 5). The neutralized stock was then given a water wash with the drum door open for 15 minutes at 50° C.
- 6). The drum was then drained
- 7). The bluestock was then treated with a standard retan and/or an amphiphilic copolymer. See each Example for the details of the specific treatment used at this step.
- 8). The stock was then offered 0.5% of powdered Pyrazol Orange Dye and drumming was continued for 20 minutes 55 at 50° C
- 9). The stock was then offered the silicone/amphiphilic copolymer composition. See each Example for the specific details. The product was predispersed in 50% float at 50 C, and drumming was continued for 30 to 60 minutes.
- 10). The stock was then offered 1.5% of 88% strength formic acid in 300 grams of water. The formic acid solution

was added in 3 aliquots spaced 5 minutes apart. Drumming was continued for a total of 30 minutes.

11). The drum was drained.

12). The stock was given a water wash with the drum door open for 15 minutes at 35°C.

13). A sample strip from the neck section of the stock was then horsed.

14). To the stock was added 5% Wayne Tan 150 (Chrome Tanning Agent) in 200% float. Drumming was continued for 60 minutes at 35° C. This step is referred to as the Cap step.

15). The drum was drained and the float collected for proper disposal.

16). The stock was given a water wash with the door open for 15 minutes.

17). The drum was drained.

18). The stock was horsed overnight. It was set out the following day (to squeeze water out of it) and vacuum dried at 70°C for 2 minutes.

18). The stock was then hung on a vertical perforated frame to air off overnight.

19). The dried leather (crust) was staked (mechanically softened) and put in a constant temperature (72° F) and humidity room (60% RH) for several days prior to testing it for waterproofness.

The following examples are presented to illustrate the invention and the results obtained by the test procedures.

EXAMPLE 1. Effect of level of aqueous dispersion of silicone oil on waterproofing. Preparation of Sample 1. An aqueous dispersion of dimethylpolysiloxane Dow Coming 200 (R) 100CS1 silicone oil (Dow Coming Corp.) was prepared using an amphiphilic copolymer emulsifier composed of 70 Cetyl-eicosyl methacrylate/30 acrylic acid having a weight average Mw= 8500 at a ratio of silicone oil:amphiphilic copolymer = 2:1 and used to treat bluestock at three different levels. In addition all samples of the blue stock were simultaneously treated with 12% of another amphiphilic polymer. Exceptions to the preparation of leathers procedure herein were:

Step 3. Used 1.75% sodium bicarbonate.

Step 7. Applied 4.3% solids of amphiphilic copolymer that was predispersed in 100% float. Drummed 60 minutes at 50° C.

Step 9. Dispersed the silicone/amphiphilic copolymer emulsion in 50% float. Drummed 60 minutes.

Table 1.1

| Waterproofing leather with various levels of aqueous dispersion of silicone oil. | | | |
|--|-----------------|----------------|---------------|
| Sample-Level | LeatherPosition | % Water Uptake | Maeser Flexes |
| Comparative A - 0.4% Solids | Middle | 37.1, 38.1 | 6,001 |
| | Butt | 32.2, 33.0 | 82,260 |
| | Average | 35.1+/-2.9 | |
| Sample 1.1 1.2% Solids | Middle | 24.6, 26.3 | 119,914 |
| | Butt | 27.8, 26.5 | >131,631 |
| | Average | 26.3+/-1.3 | |
| Sample 1-2 0.8% Solids | Middle | 26.8, 25.8 | 71,068 |
| | Butt | 26.3, 26.6 | 76,571 |
| | Average | 26.4+/-0.4 | |

Samples 1.1 and 1.2 of this invention exhibited good waterproofing relative to Comparative A in which the treatment level was below 0.5 weight percent based on leather weight.

EXAMPLE 2. Effect of level of aqueous dispersion of silicone oil on waterproofing. Preparation of Sample 2. An aqueous dispersion of silicone oil (MQ resin) formed by combining mono- and tetra- SiO-functional units dissolved in dimethylpolysiloxanes (Wacker Chemie; VP 1481) was prepared using an amphiphilic copolymer emulsifier composed

of 70 Cetyl-eicosyl methacrylate/30 acrylic acid having a weight average Mw=8500 at a ratio of silicone oil:amphiphilic copolymer = 2:1 and used to treat bluestock at two different levels. In addition all samples of the blue stock were simultaneously treated with 12% of another amphiphilic polymer. Exceptions to the preparation of leathers procedure herein were:

Step 3. Used 1.75% sodium bicarbonate.

Step 7. Applied 4.3% solids amphiphilic copolymer that was predispersed in 100% float. Drummed 60 minutes at 50° C.

Step 9. Dispersed the silicone/amphiphilic copolymer emulsion in 50% float. Drummed 30 minutes.

Table 2.1

| Waterproofing leather with various levels of aqueous dispersion of silicone oil. | | | |
|--|----------|----------------|---------------|
| Sample | Position | % Water Uptake | Maeser Flexes |
| Comparative B | Middle | 57.0, 57.0 | 5,192 |
| 0.4% VP 1481 | Butt | 37.2, 36.7 | 7,748 |
| | | | |
| Sample 2-1 | Middle | 24.6, 24.8 | 29,055 |
| 0.8% VP 1481 | Butt | 35.2, 39.3 | 18,751 |

Sample 2-1 of this invention exhibited good waterproofing relative to Comparative B in which the treatment level was below 0.5 weight percent based on leather weight.

EXAMPLE 3. Waterproofing leather with an aqueous dispersion of a functional polyorganosiloxane. Preparation of Sample 3. An aqueous dispersion of an aminofunctional polyorganosiloxane of MW= approx. 15,000 (Wacker Silicones Corp., Silicone Fluid 1434M) was prepared using an amphiphilic copolymer emulsifier composed of 70 Cetyl-eicosyl methacrylate/30 acrylic acid having a weight average Mw=8500 at a ratio of silicone oil:amphiphilic copolymer = 1:3 and used to treat bluestock. Exceptions to the preparation of leathers procedure herein were:

Step 3. Used 2.0% sodium bicarbonate.

Step 7. Applied 2.2% solids amphiphilic copolymer that was predispersed in 100% float. Drummed 60 minutes at 50° C.

Step 9. Dispersed the silicone/amphiphilic copolymer emulsion in 100% float. Drummed 60 minutes.

Table 3.1

| Leather Performance | | | |
|---------------------|----------|----------------|---------------|
| Sample | Position | % Water Uptake | Maeser Flexes |
| 3 | Middle | 33.8, 32.4 | 34,085 |
| 3 | Butt | 40.4, 37.4 | 78,869 |
| Average | | 36.0+/-3.6 | 56,477 |

Sample 3 of this invention provided good waterproofing of leather.

EXAMPLE 4. Waterproofing leather with an aqueous dispersion of silicone oils of various molecular weights (various viscosities). Preparation of Samples 4. An aqueous dispersion of DC 200/100CSt silicone oil (Sample 4.1) or DC 200/500 CSt (Sample 4.2) (Dow Corning Corp.) was prepared using an amphiphilic emulsion copolymer emulsifier composed of 80 2-Ethylhexyl acrylate/20 acrylic acid having a weight average Mw=15,000 at a ratio of silicone oil:amphiphilic copolymer = 1:3 and used to treat bluestock. Exceptions to the preparation of leathers procedure herein were:

Step 3. Used 1.75% sodium bicarbonate.

Step 7. Applied 0.84% solids of a commercial polyacrylic acid retanning agent that was dissolved in 100% float. Drummed 30 minutes at 50° C.

Step 9. Dispersed the Silicone/Amphiphilic Copolymer emulsion in 100% float. Drummed 60 minutes.

Table 4.1

| Testing of Treated Leather | | | |
|----------------------------|----------|----------------|---------------|
| Sample | Position | % Water Uptake | Maeser Flexes |
| 4.1 | Middle | 24.4, 25.5 | 84,490 |
| 1.29 % DC 200/100 CSt | Butt | 26.0, 26.8 | >128,284 |
| Average | | 25.7+/-1.0 | |
| 4.2 | Middle | 26.0, 25.3 | >128,284 |
| 1.29 % DC 200/500 CSt | Butt | 26.8, 26.8 | 125,604 |
| Average | | 26.2+/-0.7 | |

Samples 4.1 and 4.2 of this invention provided good waterproofing of leather.

EXAMPLE 5. Waterproofing leather with an aqueous dispersion of silicone oil of various silicone oil molecular weights (various viscosities). Preparation of Samples 5. An aqueous dispersion of Dow Corning 200 (R) 500CSt silicone oil (Sample 5.1) or DC 200/100 CSt (Sample 5.2) (Dow Corning Corp.) was prepared using an amphiphilic copolymer emulsifier composed of 70 Cetyl-eicosyl methacrylate/30 acrylic acid having a weight average Mw=8500 at a ratio of silicone oil:amphiphilic copolymer = 4:1 and used to treat bluestock. Comparative Sample C was prepared using the same amounts of all ingredients, including the amphiphilic copolymer used to disperse the silicone oil but without the silicone oil used in Samples 5.1 and 5.2. Exceptions to the preparation of leathers procedure herein were:

Step 3. Used 1.75% sodium bicarbonate for 2 hours.

Step 7. Applied 0.84% solids of a commercial polyacrylic acid retanning agent (LEUCKOTAN(R) 1084) which was dissolved in 100% float. Drum 30 minutes at 50 C. Thereafter, applied to the stock 4.3% solids of amphiphilic copolymer which was predispersed in 50% float. Drummed 60 minutes at 50° C.

Step 9. Dispersed the silicone/amphiphilic copolymer product in 100% float. Drummed 60 minutes.

Table 5.1

| Testing of treated leather | | | |
|----------------------------|----------|----------------|---------------|
| Sample | Position | % Water Uptake | Maeser Flexes |
| 5.1 | Middle | 17.8, 17.6 | >154,229 |
| 5.1 | Butt | 16.2, 16.6 | >127,079 |
| Comparative C | Middle | 18.0, 17.9 | 34,645 |
| Comparative C | Butt | 16.9, 17.3 | 35,775 |
| 5.2 | Middle | 17.8, 18.1 | >154,228 |
| 5.2 | Butt | 16.8, 16.9 | 99,729 |

Samples 5.1 and 5.2 of this invention exhibit waterproofing superior to that of Comparative Sample C in which silicone oil is absent.

EXAMPLE 6. Waterproofing leather with an aqueous dispersion of a polysiloxane. Preparation of Sample 6. An aqueous dispersion of a polyorganosiloxane (Dow Corning 200 (R) Fluid/100 CSt was prepared using an amphiphilic copolymer emulsifier DENSODRIN (R) BA, a product of BASF, believed, on the basis of applicants' analysis, to be composed of a hydrophobic C₂₀-C₂₄ alpha-olefin and maleic acid (1:1 molar ratio) having a weight average Mw=20,000 (soluble components) at a ratio of silicone oil:amphiphilic copolymer = 2:1 and used to treat bluestock. Comparative _

was prepared in the same manner without the silicone/amphiphilic copolymer emulsion. Exceptions to the preparation of leathers procedure herein were:

Step 3. Used 1.75% sodium bicarbonate for 2.5 hours.

Step 7. Applied 0.84% solids of a commercial polyacrylic acid retanning agent which was dissolved in 150% float. Drummed 30 minutes at 50° C. Thereafter, applied to the stock 4% solids of amphiphilic copolymer which was predispersed in 100% float. Drummed 60 minutes at 50° C.

Step 8. No dye was used.

Step 9. Dispersed 2.4% silicone/amphiphilic copolymer emulsion in 50% float. Drummed 60 minutes.

Table 6.1

| Leather Performance | | | | |
|---------------------|----------|----------------|-----------|---------------|
| Sample | Position | % Water Uptake | Softness | Maeser Flexes |
| 6 | Neck | 20.8, 21.3 | | >131,463 |
| 6 | Middle | 21.1, 19.7 | | 87,452 |
| 6 | Butt | 19.7, 20.7 | | 92,684 |
| Average | | 20.6+/-0.7 | 5.6+/-0.3 | |
| Comparative D | Neck | 22.9, 22.2 | | 12,162 |
| Comparative D | Middle | 23.2, 23.3 | | 59,437 |
| Comparative D | Butt | 22.9, 20.9 | | 13,109 |
| Average | | 22.6+/-0.9 | 5.3+/-0.4 | |

Sample 6 of this invention provided good waterproofing of leather without significant change in softness of the leather.

Claims

1. A method for waterproofing tanned leather by treating said leather with a composition comprising from 0.5 to 20 weight percent solids based on the weight of said leather of an aqueous dispersion of a silicone oil emulsified with a water-insoluble amphiphilic copolymer, said copolymer formed from 50 weight percent to 90 weight percent, based on the weight of said copolymer, of at least one ethylenically-unsaturated hydrophobic monomer selected from monomers consisting of hydrophobic alkyl (meth)acrylates; primary alkenes; vinyl esters of alkyl carboxylic acids; vinyl alkyl ethers; dialkyl esters, alkyl ester N-alkylamides, diN-alkylamides, hemi alkylesters, or hemi N-alkylamides of unsaturated dicarboxylic acids; and from 10 weight percent to 50 weight percent, based on the weight of said copolymer, of at least one copolymerizable water-soluble ethylenically-unsaturated acidic or basic hydrophilic comonomer; wherein said copolymer has a weight average molecular weight of from 2000 to 100,000; and wherein the ratio of silicone oil to amphiphilic copolymer by weight is from 1: 5 to 8:1.
2. The method of claim 1 wherein said hydrophobic monomer is selected from the group consisting of C₂-C₂₂ alkyl (meth)acrylates, and mixtures thereof.
3. The method of claim 1 wherein said hydrophobic comonomer further comprises less than 50 weight percent of one or more hydrophobic comonomers selected from the group consisting of styrene, methylstyrenes, vinyl acetate, (meth)acrylonitrile, N-alkyl(meth)acrylamides, and olefins.
4. The method of claim 1 wherein said hydrophilic monomer is selected from the group consisting of (meth)acrylic acid, and mixtures thereof.
5. The method of claim 1 wherein wherein the ratio of silicone oil to amphiphilic copolymer by weight is from 1: 3 to 4:1.

6. An aqueous composition for use in waterproofing leather comprising an aqueous dispersion of a silicone oil emulsified with a water-insoluble amphiphilic copolymer, said copolymer formed from 50 weight percent to 90 weight percent, based on the weight of said copolymer, of at least one ethylenically-unsaturated hydrophobic monomer selected from monomers consisting of hydrophobic alkyl (meth)acrylates; primary alkenes; vinyl esters of alkyl carboxylic acids; vinyl alkyl ethers; dialkyl esters, alkyl ester N-alkylamides, diN-alkylamides, hemi alkylesters. or hemi N-alkylamides of unsaturated dicarboxylic acids; and from 10 weight percent to 50 weight percent, based on the weight of said copolymer, of at least one copolymerizable water-soluble ethylenically-unsaturated acidic or basic hydrophilic comonomer; wherein said copolymer has a weight average molecular weight of from 2000 to 100,000; and wherein the ratio of silicone oil to amphiphilic copolymer by weight is from 1: 5 to 8:1.
7. The composition of claim 6 wherein said hydrophobic monomer is selected from the group consisting of C₂-C₂₂ alkyl(meth)acrylates, and mixtures thereof.
8. The composition of claim 6 wherein said hydrophobic comonomer further comprises less than 50 weight percent of one or more hydrophobic comonomers selected from the group consisting of styrene, methylstyrenes, vinyl acetate, (meth)acrylonitrile, N-alkyl(meth)acrylamides, and olefins.
9. The composition of claim 6 wherein said hydrophilic monomer is selected from the group consisting of (meth) acrylic acid, and mixtures thereof.
10. The composition of claim 6 wherein wherein the ratio of silicone oil to amphiphilic copolymer by weight is from 1: 3 to 4:1.